Literature Survey of Corrosion Prevention
in Idle Boilers

Assignment 73 120
MEL R&D Phase Report 116/66
Sub-Project S-F020 02 02
Task 0613
April 1966

By
A. H. Wirzburger

U. S. NAVY

MARINE ENGINEERING LABORATORY

Annapolis, Md.

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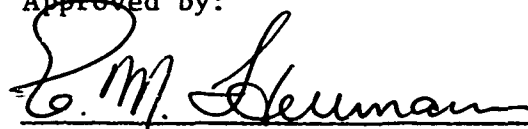
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ABSTRACT

A survey of the literature was conducted to gain
insight into the possibility of finding a chemical
additive that will prevent corrosion in idle boilers
yet still allow them to be returned to operation with-
out first requiring draining. The mechanisms of cor-
rosion and the important factors which affect boiler
corrosion are discussed. Corrosion inhibitors are
classified by the mechanisms they employ for protection.
Future work to be conducted is based upon the results
of this survey.

ADMINISTRATIVE INFORMATION

The work reported herein was performed under MEL Assignment 73 120, Sub-Project S-F020 02 02, Task 0613. It is part of the planned program on Water Treatment described in MEL Program Summary dated 1 November 1965.
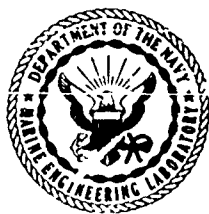
UNITED STATES NAVY

MARINE ENGINEERING LABORATORY

ANNAPOLIS, MARYLAND — 21402

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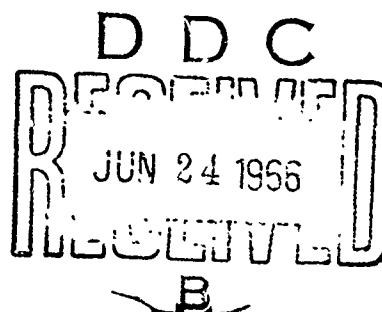By direction

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LITERATURE SURVEY OF CORROSION PREVENTION
IN IDLE BOILERS

1.0 INTRODUCTION

As part of this Laboratory's program for developing improved treatments for Naval boilers, a study aimed at the development of a treatment which can be applied to idle boilers is being undertaken. This treatment is required to prevent corrosion while the boilers are not being operated and still allow them to be returned to operation without first draining the chemical additive. A literature survey was conducted to determine what work has been done in this field. This report summarizes the results of this survey.

The information for this report was obtained from a search of the published literature and through personal contacts with authorities in the field of corrosion.

The following abstracts were reviewed:

- The Engineering Index (1940-1964)

- Chemical Abstracts, American Chemical Society (1937-1965)

- D. D. C. Bibliography, ARB-NO 037248

- Patent Search

In addition to the abstracts and bibliographies, the following journals were searched:

- Corrosion (1947-1965), National Association of Corrosion Engineers

- Power Engineering (1960-1964), Technical Publishing Company

- Industrial and Engineering Chemistry (1940-1964), American Chemical Society

1.1 Scope. This survey was conducted to study the mechanisms and corrosion products that are most often encountered with carbon steel under conditions that are likely to be encountered in 1200 psi* boilers in both operating and idle conditions. The majority of findings of this survey apply equally to low pressure boilers as well, with some changes in relative efficiencies expected. This survey was limited to literature describing the prevention of corrosion products most often found on carbon steel[1] (magnetite (Fe_3O_4)) and three forms of basic ferric oxide (FeOOH or $Fe_2O_3 \cdot H_2O$) with no great concern for any other deposits formed under unusual conditions.

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*Abbreviations used in this text are from the GPO Style Manual, 1959, unless otherwise noted.
[1]Superscripts refer to similiarly numbered entries in the Bibliography.

2.0 PROCESS OF BOILER CORROSION[2]

Simply, boiler tube corrosion can be described as an electrolytic process occurring when a metal such as iron is exposed to a conducting medium (electrolyte) such as water. During this process at room temperature, iron goes into solution at the anode to form ferrous ions; electrons flow to the cathode where they reduce hydrogen ions from the boiler water to form hydrogen atoms. The hydrogen atoms collect on the cathode, thereby stifling the reaction and preventing the occurrence of pitting at the anode. If, however, dissolved oxygen is present or if the pH is low, the hydrogen atoms are removed from the surface of the cathode and pitting corrosion continues until the boiler tube is perforated.

The limiting rate in a corroding system is established when the total polarization potential E_T' equals the total cell driving force or open-circuit potential between anodic and cathodic area, E_0.

$$E_T' = E_a' + E_c' + I(R_\ell + R_i) = E_0 \text{ - - - - - - - - - - - (1)}$$

Metal circuit resistance, R_ℓ, is usually negligible. Rearranging Eq. (1) yields an expression for the corrosion current which is directly proportional to the corrosion rate.

$$I = \frac{E_0 - (E_a' + E_c')}{R_i} \text{ - - - - - - - - - - - - - - - - - (2)}$$

The current (I) can be reduced by reducing E_0 or by increasing electrolyte resistance R_i, anode polarization E_a' or cathode polarization E_c'. To reduce E_0 we can make the metal surface more homogeneous, thereby reducing the inequities between anodic and cathodic areas, by surface polishing, or heat treatment. Usually this approach is inconvenient in existing equipment. Although some inhibitors function by reducing E_0, the usual approach is to add substances which serve to increase E_a' or E_c' or both. This is accomplished at the electrode sites by establishing concentration polarization, by creating or enhancing surface films, by promoting overvoltage, or by a combination of these effects.

Two dissimilar metals in electrical contact and immersed in a conducting solution can form an electrolytic cell. The less noble of the two metals becomes the anode and corrodes, whereas the other metal becomes the cathode and is therefore protected. For example, iron is protected by magnesium in sodium chloride solutions.

When a single metal or alloy corrodes, local electrolytic cells generally operate on its surface. Some parts of the metallic surface serve as anodes, and others as cathodes. The distribution of the anodic and cathodic areas depends upon such factors as the energetics of the various parts of the surface (crystal-lattice imperfections, strains, etc.), the distribution of surface contaminants (layers of adsorbed substances or insoluble metal compounds), and

2

the environmental conditions (access of the corrosive medium, air, or other gases to the various parts of the surface). The quantity of electricity (current) flowing through the local cells is equivalent to the amount of metallic corrosion in accordance with Faraday's law.

As electrical current begins to flow through a local cell, the potential of the anode and the potential of the cathode (A and C, respectively, in Fig. 1, I) shift closer to each other, i.e., become polarized. The anodic potential shifts toward more cathodic values and the cathodic toward more anodic values. At "a" the potential of the anode and the cathode approach each other and this represents the maximum current that can flow under these experimental conditions and this corresponds to the maximum steady-state corrosion theoretically possible.

Conditions which decrease the slopes of the polarization curves, i.e., shift the convergence point of anodic and cathodic potential to higher current values, will result in acceleration of corrosion (Figs. I, II and III); shifting to lower current values will result in inhibition of corrosion. Corrosion inhibitors retarding the anodic reaction cause anodic polarization and the anodic curve becomes Ad (Fig. 1, IV); if the cathodic reaction is retarded the cathodic curve becomes Ce (Fig. 1, V) and if both anodic and cathodic reactions are retarded the curves are Af and Cf (Fig. 1, VI).

2.1 <u>Selective Corrosion (Pitting)</u>.[3] If carbon steel corroded uniformly in boiler water, corrosion would become a relatively simple problem. A simple calculation would reveal the lifetime of the tube once the minimum tolerable thickness was established. Unfortunately selective attack occurs.

There are two major types of pitting; low-temperature pitting and on-load pitting.

2.1.1 Low-Temperature Pitting. There are two types of low-temperature pitting--"air bubble" and "soft scab" pitting.

Air-bubble pitting occurs during idle periods when the boiler is filled with cold water containing a substantial amount of dissolved oxygen (See Fig. 2). Daily fluctuations in temperature presumably cause dissolved air to leave solution where it collects as bubbles on the metal surface. A differential aeration cell then results with corrosion initially occurring in the anodic area at the outside periphery at the bubble-metal interface, where oxygen concentration is the lowest. Eventually the oxygen within the bubble is consumed, while at the same time a thin shell of corrosion product is built up over the surface originally covered by the bubble. The aeration cell then is reversed - the higher oxygen content is in the bulk solution, and the area beneath the bubble begins to pit. Pitting continues as long as the porous corrosion products permit passage of ions but restrict the diffusion of oxygen.

Figure 1
Theoretical Polarization Curves
(Potential vs Current)
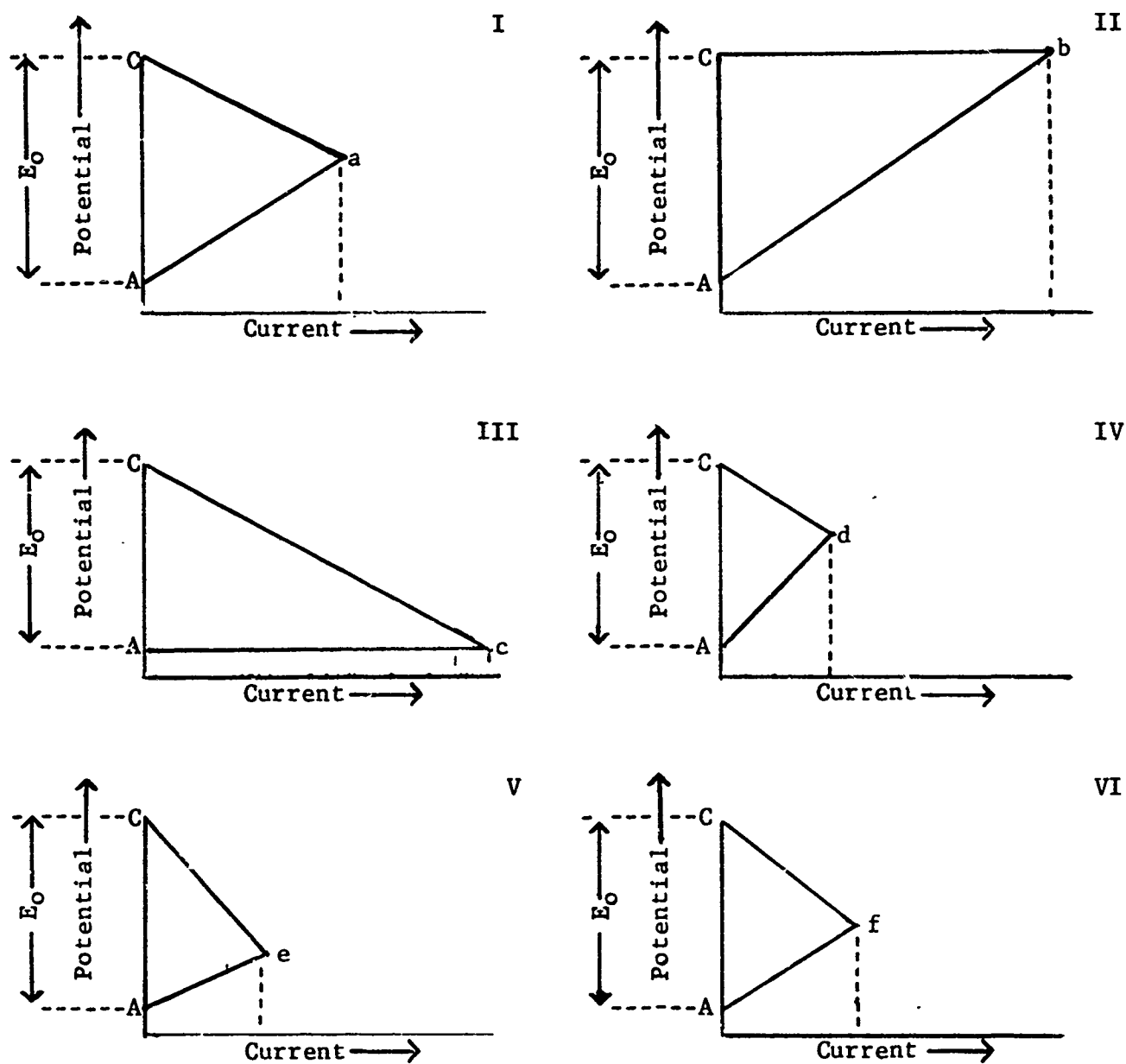
E_O = open circuit potential
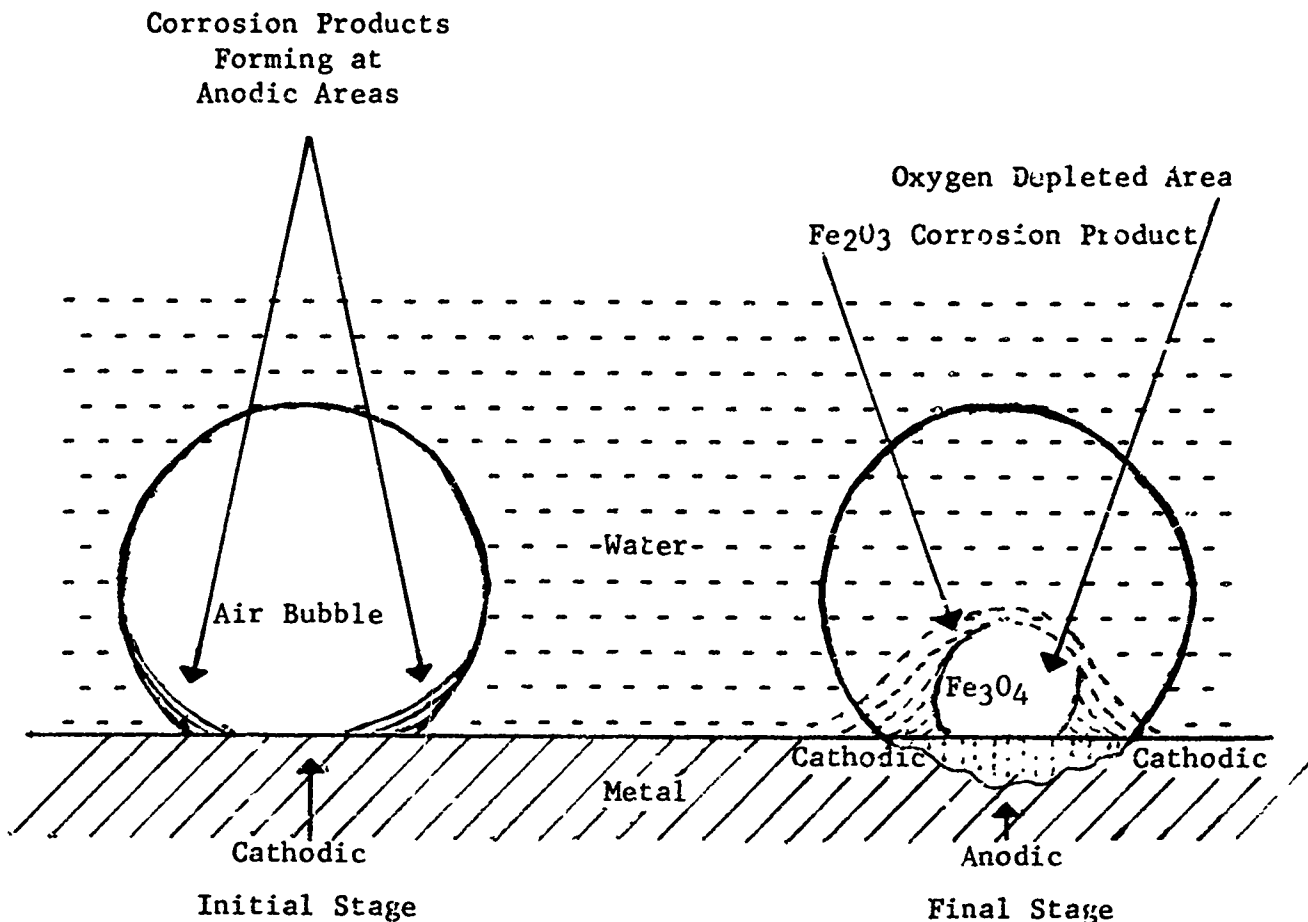
Figure 2
Air-Bubble Pitting[4]

Soft scab pitting occurs in areas which are above the water line, but occasionally come in contact with boiler water. Subsequent evaporation apparently results in deposition of salts from the water. During shutdown, the humid conditions within the boiler can cause drops of condensate to form. These redissolve the salts to form a concentrated electrolyte which then causes pitting to occur beneath the bubble because of differential aeration. A soft scale containing appreciable red iron oxide (Fe_2O_3) builds up over the pit. This type attack may take place any time suitable conditions exist. Alternate layers of α Fe_2O_3 and Fe_3O_4 found in boiler-tube pits have been related to corrosion at ambient temperature. The layers were believed to have resulted from γ or α FeOOH forming in cold aerated distillate and then converting to α Fe_2O_3. The Fe_3O_4 was thought to have formed from $NaFeO_2$ decomposition.

2.1.2 On-Load Pitting. On-load pitting is characterized by the build up of
dense layers of Fe_3O_4 in the pit. The cause of this pitting is not definitely
known. Many theories have been advanced; namely, local overheating of the
metal, localized concentration of caustic, localized separation of the Fe_3O_4
film caused by thermal gradient stresses, dissolved oxygen, dissolved carbon
dioxide, or copper in the solution.

3.0 FACTORS AFFECTING BOILER CORROSION

A review of the available literature was made to determine how the fol-
lowing factors will affect boiler corrosion.

3.1 Velocity.[5] Generally corrosion increases with velocity, but the effect
could be just the opposite. A little motion tends to keep conditions uniform
throughout the solution and tends to make corrosion uniform over the entire
metal surface, thereby preventing local attack. Motion may also set up turbu-
lence producing non-uniform conditions that, in turn, may lead to pitting.
Motion generally increases total weight loss by supplying corrosives to the
metal surface at a faster rate, although this same motion may create just the
opposite effect by supplying inhibitors to dead spaces. In general, however,
the more motion, the more corrosion.

3.2 Temperature.[6] The corrosion rate for steel in a closed system saturated
with air increases linearly on the order of 3% per degree from 0 to 100C. Rate
increases from 20 to 30% per 10 C rise are typical of diffusion-controlled
processes. A major effect of temperature change in aqueous environments is
the variation of oxygen and carbon dioxide solubility. As the temperature
increases, the solubilities of oxygen and carbon dioxide decrease, thereby
reducing corrosion from this cause.

The components of a solution also respond to temperature change. The
dissociation of water increases at higher temperature, and though the change
is not too great, it can be significant (Fig. 3). For steel, the corrosion
rate in water at 22 C is constant from pH 4 to about 10, rising on the acidic
end and decreasing on the alkaline end. At 40 C a constant rate of corrosion
is obtained from a pH of 4.5 to 8.5. This reflects the enhanced activity of
the hydrogen ion in raising the rate of corrosion on the low pH side and the
activity of the hydroxyl ion in passivating the steel on the alkaline side.
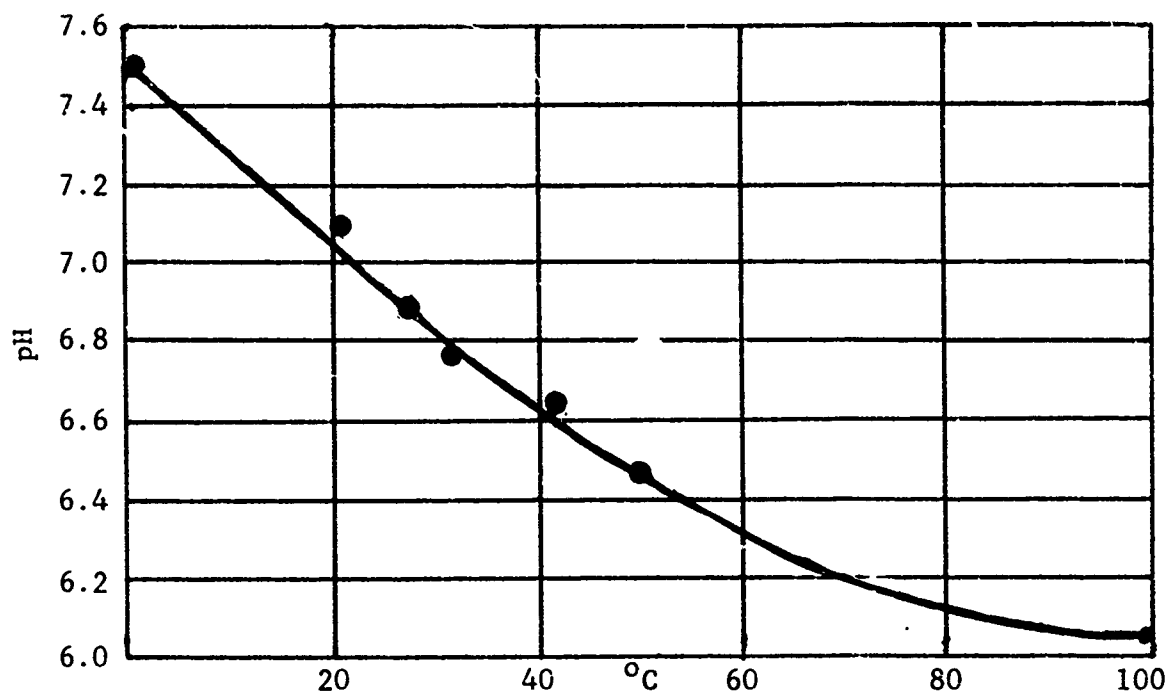
Figure 3
Change of pH of Water with Temperature [6]

3.3 <u>Hydrogen Ion Concentration (pH)</u>. In general, the lower the pH, the higher the rate of corrosion. This condition is dependent on temperature, pressure, and the characteristics of the solution remaining constant. From the stand-point of factors controlling the corrosion and rate of reaction of iron, aqueous solutions are of three types; acid, neutral, and alkaline.[7] "In acidic solutions, the reaction produces hydrogen evolution and continues without form-ing protective films of corrosion products. The controlling factors are total acidity and hydrogen-ion concentration, with aeration playing a minor role."

In the neutral range, iron has a relatively poor resistance, as a film con-tinues to develop for a period of years in an aerated aqueous solution. This film rapidly slows the corrosion rate by suppressing hydrogen evolution. Hydrogen evolution is also suppressed by the lowered total acidity and hydrogen-ion concentration. Corrosion rates in this range are controlled by the diffusion of oxygen through the film and are relatively independent of the hydrogen-ion concentration.

Alkaline solutions have only a slight corrosive action on iron because of the development of a protective corrosion product film. The films in the alkaline range are more effective than in the neutral range. The resistivity to corro-sion increases with alkalinity and hydroxyl-ion concentration. Aeration has a much smaller effect on the corrosion rate of alkaline solutions than on that of neutral solutions with the effect decreasing rapidly above a pH of 9.

In acid or alkaline solutions, the attack is normally uniform, whereas in neutral solutions pitting occurs.

3.4 **Dissolved Oxygen**.[8] Corrosion rates of steel in oxygenated water are approximately proportional to the oxygen concentration if it is below 5.5cc per liter, while at higher concentrations the rates of corrosion are considerably lower than those demanded by a strict adherence to the linear relationship. Conditions which tend to increase the amount of dissolved oxygen in the solution (low temperature, high pressure, etc.) lead to an increased rate of corrosion, whereas those that decrease the oxygen concentration (sulfite, hydrazine, etc.) tend to decrease it.

The decrease in the differential corrosion rate as oxygen concentrations become greater is due to the gradual formation of corrosion products of a type which exhibits a greater resistance to the transfer of oxygen.

At low oxygen concentrations the corrosion products formed consist largely of a granular black magnetic oxide of iron which is not resistant to the transfer of oxygen, while at higher oxygen concentrations the protective gelatinous ferric hydroxide is formed.

At low oxygen concentrations the rate of oxidation of ferrous ions to ferric ions is slow enough to permit the precipitation of both the ferrous and ferric hydroxides with the subsequent formation of magnetic oxide. On the other hand, at high oxygen concentrations the rate of oxidation of ferrous ions to ferric is high enough to prevent the accumulation of ferrous ions so that only the protective ferric hydroxide is precipitated. The two reactions

$$2H^+ + 2e^- \rightarrow H_2 \ \text{-------------------------} \ (3)$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \ \text{----------------} \ (4)$$
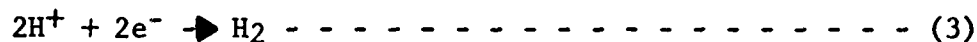
control the rate at which iron corrodes. The latter reaction is so rapid that the oxygen concentration at the metal surface approaches zero, and the rate at which depolarization proceeds depends on the rate of diffusion of oxygen through the stagnant film at the metal surface. This diffusion rate is proportional to the oxygen concentration in the attacking medium, which results in the corrosion rate being proportional to the total oxygen concentration.

3.5 **Carbon Dioxide**. The corrosion rate of steel increases with the percent of carbon dioxide dissolved in the water. Carbon dioxide dissolved in water increases the acidity by reaction (5).

$$2CO_2 + 2H_2O + 2e^- \rightarrow 2HCO_3^- + H_2 \ \text{-----------} \ (5)$$
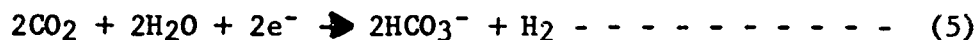
Although the concentration of CO_2 is important, at 60 C O_2 is 6 to 10 times more corrosive than the same amount of CO_2.

4.0 CORROSION INHIBITORS

Corrosion inhibitors may be listed in several groups depending on the mechanism they employ to inhibit corrosion. These mechanisms can be divided into five basic classes:

● Those which raise the pH of the solution, thereby reducing the hydrogen ion activity.

● Those which act as oxygen scavengers, thereby removing the dissolved oxygen from the solution.

● Those which remove the carbon dioxide from the solution, thereby raising the pH of the solution.

● Those which form a protective film, thereby preventing the corrosive constituents of the solution from reaching the surface of the metal.

● Those which function by virtue of an adsorbed layer, thereby forming a non-reactive layer on the surface of the metal.

Most corrosion inhibitors employ combinations of two or more of these classes in preventing metal corrosion.

4.1 **Oxygen Scavengers**.[9] Oxygen scavengers are used to prevent corrosion because they prevent the reaction

$$2H_2 + O_2 \rightarrow 2H_2O \text{ - - - - - - - - - - - } \tag{6}$$
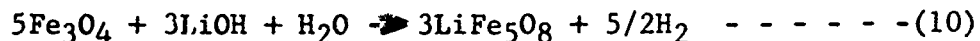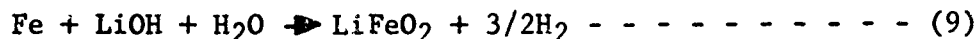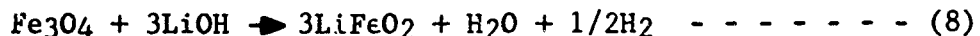
from taking place at the cathode. This allows an insulating blanket of hydrogen to stay on the cathode which results in polarization. Polarization interferes with the current flow, so that the corrosion is decreased or stopped. If the insulating blanket of hydrogen is removed from the cathode by the dissolved oxygen in the water, then cathodic depolarization results, current flows and corrosion proceeds.

There are two basic oxygen scavengers now used in the treatment of boiler water and the choice between these two depends primarily on whether or not the boiler contains a nondrainable superheater to be protected. If there is no nondrainable superheater, catalyzed sodium sulfite is the most appropriate chemical and this is used in the range of 100-200 ppm. If there is a nondrainable superheater and flooding is to be used for standby protection, the oxygen scavenger must be volatile so that no deposits are formed in the superheater when the boiler is returned to service. The only suitable oxygen scavenger for this type protection seems to be hydrazine.[10] Hydrazine has the added advantage that it is also an appropriate alkali and this helps to raise the pH to about 9.5. This usually requires about 250 ppm of hydrazine.

4.2 **pH Adjustors**. The choice of an alkali to adjust the pH of the boiler water is also dependent on whether or not there is a nondrainable superheater to be protected. If there is no nondrainable superheater, caustic soda is

the most appropriate chemical, with the alkalinity maintained between 400-500 ppm NaOH.

Concentration of alkaline solutions during steam generating processes is a major cause of boiler failures due to pitting. Bloom[11,12,13] reported that in a concentrated LiOH solution, a protective film consisting of a mixture of Fe_3O_4 and a high temperature form of $LiFeO_2$ is formed from the reactions:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \text{ - - - - - - - - - - - - - - - (7)}$$

$$Fe_3O_4 + 3LiOH \rightarrow 3LiFeO_2 + H_2O + 1/2H_2 \text{ - - - - - - - (8)}$$

$$Fe + LiOH + H_2O \rightarrow LiFeO_2 + 3/2H_2 \text{ - - - - - - - - - - - (9)}$$

$$5Fe_3O_4 + 3LiOH + H_2O \rightarrow 3LiFe_5O_8 + 5/2H_2 \text{ - - - - - -(10)}$$

The most significant fact seems to be the low concentration at which reaction (9), the formation of $LiFeO_2$, occurs in the LiOH system. It is surprising to find $LiFeO_2$ deposited by 1 percent LiOH in view of the fact that NaOH and KOH are still generating Fe_3O_4 by reaction (7) when their concentrations are 40 and 48 percent, respectively. Because reaction (7) consumes water makes it certain that reaction of a metal surface with NaOH or KOH is accompanied by concentration of the alkali at the site of the reaction. Since the generation of $LiFeO_2$ consumes LiOH and takes place by both reactions (8) and (9), it is seen that as soon as LiOH solution is concentrated (to at least 1%) it reacts with any Fe_3O_4 or steel which it contacts, generating $LiFeO_2$ and reducing the LiOH concentration at the site of the reaction. The only method available to concentrate the LiOH would be by evaporation sufficiently rapid to overcome the consumption of LiOH by reaction with steel or Fe_3O_4.

At LiOH concentrations below 1%, where the spinel phase appears, the LiOH concentration diminishes with time. This disappearance is the result of reaction (10) in which lithium is incorporated into the spinel film. The well-known spinel $LiFe_5O_8$ was obtained at high LiOH concentrations.

The concentration of the solution determines which of the four different oxide phases are generated in the reaction of steel with LiOH solutions at 600 F. If the concentration is below 0.5% only an adherent, protective spinel-structured film is generated. At concentrations from 1 to 4.5% an adherent tight film is generated. This film consists of a spinel phase next to the steel and a low temperature form of $LiFeO_2$ overlying the spinel. The spinel phase contains lithium, and at 4.5% LiOH, gives the x-ray pattern of the lithium-saturated spinel $LiFe_5O_8$. Above 5% a corrosion product film of high temperature $LiFeO_2$ is formed. In LiOH solutions the alkali concentration at the reaction sites cannot rise to high values due to the consumption of LiOH by reactions (8), (9), and (10), except under conditions of rapid water evaporation.

This is in direct contrast to NaOH and KOH solutions which tend to concentrate rather than dilute as reaction (7) concentrates alkali at the site of the reaction. This indicates that LiOH may have distinct advantages from the standpoint of attack by concentrated alkali over the other alkalies for boiler water alkalization.

If there is a nondrainable superheater, then volatile alkalies such as cyclohexylamine, morpholine, hydrazine, and ammonia are the most commonly used and require in the range of 100 ppm of cyclohexylamine or morpholine and 250 ppm of hydrazine.

4.3 Carbon Dioxide Controllers. The percent of the total carbon dioxide present in the solution as H_2CO_3 and HCO_3^- is controlled by the pH of the solution. Therefore the same alkalies that are used to raise the pH of the solution, lower the concentration of H_2CO_3 and HCO_3^-, converting them to $CO_3^=$ which is not as corrosive.
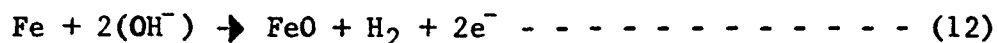
4.4 Formation of Thin Films. Most compounds used as corrosion inhibitors fall into this class. The reason is that oxide films formed on the surface protect the metal from further attack. In the corrosion of iron by water, the reactions at the solid-liquid interface are rate-determining. These reactions are classed as anodic and cathodic. Though anodic and cathodic reactions can take place at the same point, these reactions must balance, and the driving force for the reaction must distribute itself so that both go at the same rate. The reaction requiring the greater driving force (slower reaction) for a given rate is said to be rate-controlling.

4.4.1 Anodic Reaction.[14] In anodic processes, the metal passes into the ionic state. This can take place either by metal dissolution or by the direct formation of a film. For an iron-water system, the possible anodic reactions are:

Metal Dissolution

$$Fe \rightarrow Fe^{++} + 2e^- \quad\text{-----------------------------} (11)$$

Ferrous Oxide Formation

$$Fe + 2(OH^-) \rightarrow FeO + H_2 + 2e^- \quad\text{----------------} (12)$$

Ferrous Hydroxide Formation

$$Fe + 2(OH^-) \rightarrow Fe(OH)_2 + 2e^- \quad\text{----------------} (13)$$
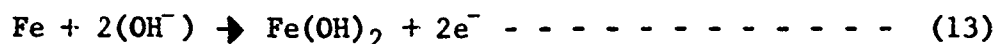
Magnetite (Fe_3O_4) formation in high temperature degassed water can take place through any of the three following reactions:

Magnetite Formation

Via Hydroxide

$$3F\acute{e}(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \text{ - - - - -- - - - - -} \quad (14)$$

Via Oxide

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \text{ - - - - - - - - - - - - -} \quad (15)$$
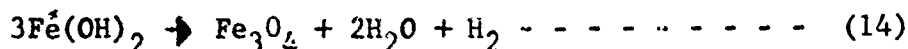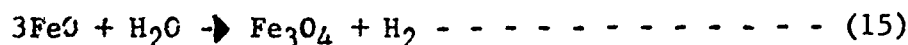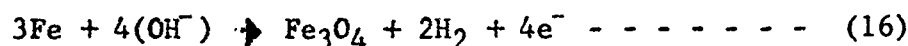
Direct from Metal

$$3Fe + 4(OH^-) \rightarrow Fe_3O_4 + 2H_2 + 4e^- \text{ - - - - - - - -} \quad (16)$$

● Anodic Inhibitors.[15] An anodic inhibitor is one that restrains the anodic corrosion reactions. If the water is sufficiently alkaline, the immediate anodic product, ferrous hydroxide, is only sparingly soluble even though it is appreciably soluble in neutral solution. Most of the anodic inhibitors are alkaline bodies such as sodium hydroxide, sodium carbonate, sodium silicate, and sodium phosphate. The special value of the last two is that they form sparingly soluble films of iron silicate or phosphate. The chromates are particularly efficient as anodic inhibitors because any ferrous salt momentarily formed will be precipitated as a mixture of hydrated ferric and chromic oxide. The addition of chromate in the range of 500-2000 ppm and caustic soda to adjust the pH to 8.5 will protect boilers in standby.

● The "Dianodic* Method"[16,17,18,19,20,21] is able to give benefits in relatively low concentrations not obtainable with single treatments such as chromate, phosphate, and silicate at considerably higher concentrations. This method eliminates the typical pitting and tuberculation that single chromate and single phosphate treatments cause when used in insufficient concentrations. These two anodic treatments act as a single agency for the elimination of pitting and tuberculation and not as two separate treatments. The phosphates used in this method, as well as those used alone, are polyphosphates[22] which have proved more effective than sodium phosphate.

Anodic inhibitors are extremely effective when added in sufficient quantity, but if the inhibitor is present in insufficient quantity, corrosion may set in locally and may be more intense than if no inhibitor had been added. The addition of an anodic inhibitor in insufficient amount may stifle corrosion over a large part of the metal surface, but allow it to proceed at the most susceptible places. If chromate[23,24,25] or phosphate[26,27,28,29] is used alone,

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*The term "Dianodic" is employed as a convenient expression to identify a specific combination of two anodic inhibitors (phosphate and chromate) in proper ratio at a controlled pH for the prevention of pitting and tuberculation.

a high concentration must be maintained during the standby period to be effective. Once the boiler is restarted, this treatment would be the cause of high solids content in the boiler water. If the boiler is blown down, the resulting low concentration of chromate or phosphate would increase the corrosion.

• Silicate treatments[21],[30] form a protective film on the metal surface and prevent the corrosive elements from reaching the metal surface. These films take several days to form completely and require constant water motion during the formation period to assure a completely uniform film. These films are used mostly where continuous injection is maintained and flow through the system is fairly continuous.

Other chemicals that fall into this group include the chrome glucosates[31] (which can not be used in water for human consumption), sodium benzoate,[32] and tetraphospho-glucosate.[33]

Another anodic inhibitor is the nitrite[34],[35],[36],[37] ion which is adsorbed at anodic areas and then reduced by hydrogen at adjacent cathodic areas to give a protective oxide layer and reduction products of nitrite. Nitrite can accelerate corrosion if an oxide solubilizer is present, as this agent prevents formation of a complete oxide layer. The dissolved oxygen concentration inversely affects the amount of nitrite required for the inhibition of steel corrosion; an increase in the oxygen concentration decreases the concentration of sodium nitrite required. A concentration of 200 ppm should be maintained at all times to protect the boiler adequately.
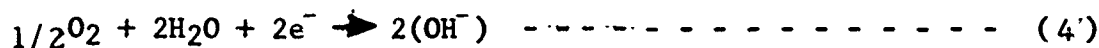
4.4.2 Cathodic Reaction. The electrons left behind in the metal by the anodic reaction must be neutralized by a corresponding cathodic reaction. If this cathodic process can be restrained or prevented, then the anodic process is likewise affected. This is an extremely important point as cathodic polarization so often determines the over-all steady corrosion rate. In degassed, pure water the only possible cathodic reaction is the discharge of hydrogen ions; thus
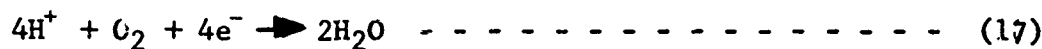
Hydrogen Evolution

$$2H^+ + 2e^- \rightarrow H_2 \quad\text{- (3)}$$

If air is present, the cathodic reaction may be molecular reduction.

Oxygen Absorption

$$1/2 O_2 + 2H_2O + 2e^- \rightarrow 2(OH^-) \quad\text{- - - - - - - - - - - - - - - - - (4')}$$

Water Discharge

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad\text{- - - - - - - - - - - - - - - - - - (17)}$$

Hydrogen ion discharge will take place if the potential of any point on the water vs solid phase interface is below the thermodynamic electrical potential of this reaction. Hydrogen evolution is dependent upon (1) the pH

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of the solution, (2) the potential of the particular film or metallic surface exposed to the solution, and (3) the overvoltage characteristics of that surface or of the inclusion contained therein.

● Cathodic inhibitors[38] restrain the cathodic corrosion reaction:

$$O_2 + H_2O + 4e^- \rightarrow 4(OH^-) - - - - - - - - - - - - - - (4)$$
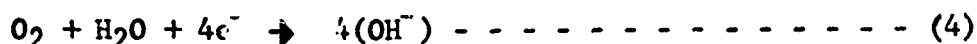
Salts of metals which form sparingly soluble hydroxides, oxides, and carbonates, such as zinc and nickel, act as cathodic inhibitors. Organic polar compounds are passivators functioning through cathodic polarization. Corrosion formed in the presence of cathodic inhibitors tends to be uniformly distributed rather than as pitting. Cathodic inhibitors do not restrain attack until a film of visible thickness has formed, but they also continue to retard corrosion even after dosage of the water with the inhibitor has been discontinued. Glassy phosphates are one class of chemical compound that works on the cathodic inhibitor principle. These films are slow to form and work efficiently as long as a residue of the phosphate remains in solution. Another chemical found suitable under some circumstances is 2-methylpiperazine[39] which has worked well as an inhibitor in the form of an aqueous fog. Many other organic substances work in a similar manner by the adsorption of the inhibitor molecule from the solution onto the metal surface.[40]

From the foregoing it appears that anodic inhibitors are efficient but dangerous (increased corrosion results if the concentration is not maintained at a high enough level), while cathodic inhibitors are inefficient but safe. Using anodic and cathodic inhibitors concurrently has been only partially successful. No one inhibitor has been found that is satisfactory under all conditions.[41]

4.5 Adsorbed Layers[42]

● Adsorbed inhibitors are generally organic nitrogen or sulfur compounds, and the majority of the fundamental investigations have been confined to compounds of this type.[43,44,45,46,47,48,49,50] Research workers have reached the tentative conclusion that a number of factors control the efficiency of an inhibitor. Some of the more important are solubility, stability toward oxidation and reduction, molecular size and shape, and electronic factors. Riggs and his associates[51] have outlined the electronic factors which control adsorption and hence corrosion inhibitions, as follows:

- Electronic structure of the metal.

- Ionization energy of the inhibitor, or its ability to donate its electrons to the metal.

- The interaction integral between the inhibitor and the metal.

- The separation of charges in the dative state.

They determined the nuclear magnetic resonance spectra of solutions of aniline and its derivatives in cyclohexane (Fig. 4).
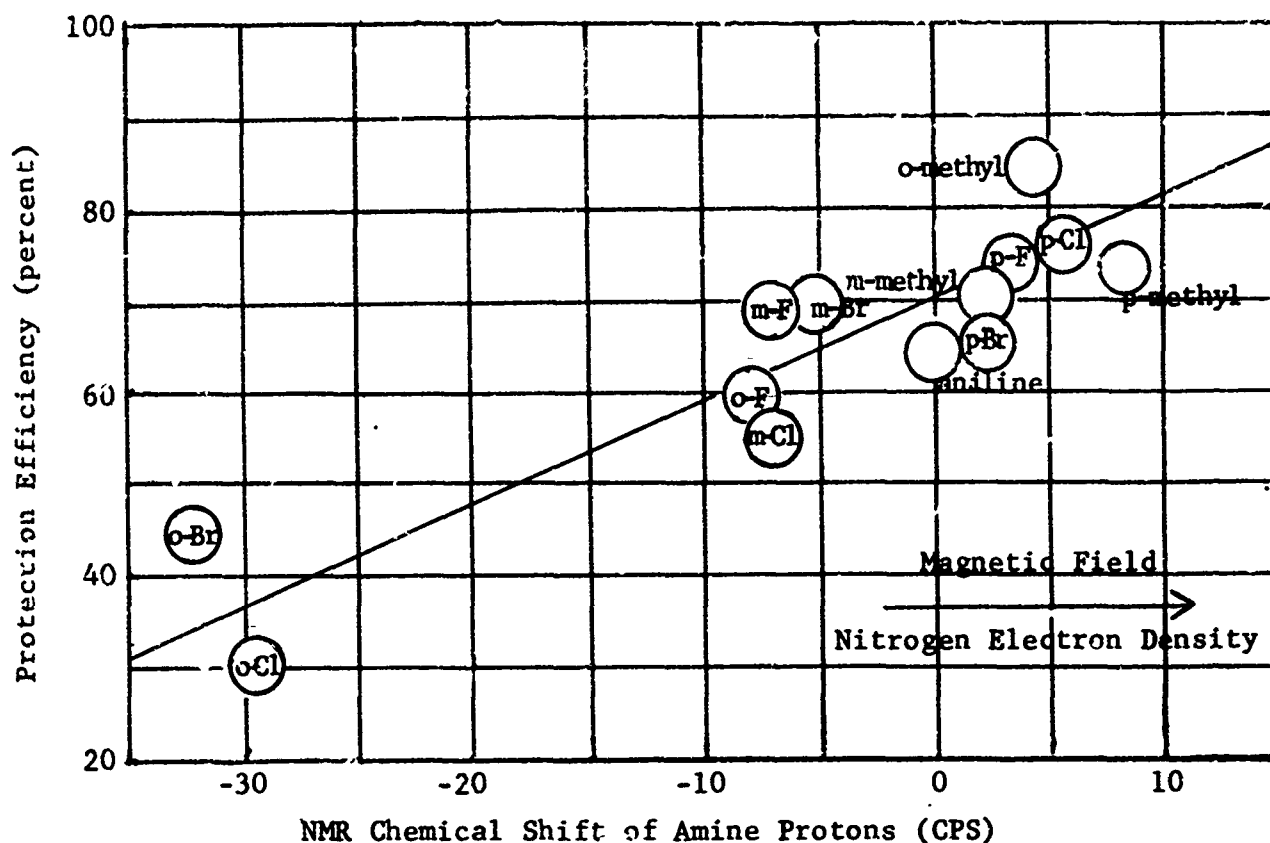
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Figure 4
Corrosion Inhibition Measured by Nuclear Magnetic Resonance[42]

The NMR frequency of amine protons is a measure of the electron density on the nitrogen atom. The chemical shift of these amine protons is related to the efficiency of aniline derivatives in inhibiting corrosion of iron in hydrochloric acid. Chlorine in the ortho position has a strong electron-withdrawing effect on the amine group and o-chloroaniline is ineffective as an inhibitor. One effective inhibitor which has an electron-contributing effect is o-toluidine. The general trend of the data showed that maximum corrosion inhibition was obtained with a positive chemical shift. Conversely minimum inhibition was observed with a negative chemical shift. The data illustrates the importance of the electron density on the nitrogen atom in the formation of a dative bond with the metal surface.

Hackerman* recently studied the inhibition efficiency of various imines and secondary amines for the corrosion of iron in HCl. He attributes the greater effectiveness of decamethyleneimine over dipentylamine to π electron character typical of aromatic rings. The sp^2 orbital in the decamethyleneimine leaves some bonding capability available for a surface bond. This surface bond, in turn, results in strong adsorption and good corrosion inhibition. Many compounds[52,53,54,55] which possess this strong adsorption tendency are good

*Hackerman's studies are referenced by Riggs[51]

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corrosion inhibitors; this applies to many systems not just those containing hydrochloric acid.

5.0 FUTURE WORK

Laboratory studies on promising inhibitors for use in 1200 psi boiler systems are being conducted. These compounds will be evaluated to determine the most effective concentration of inhibitor for maximum protection and minimum side effects. Combinations of inhibitors also will be evaluated to determine if improved results are obtained.

Appendix A

Bibliography

1 - Eberhardt, R. D., E. W. Arneson, and C. E. Imhoff, Corrosion, Vol. 17, Apr 1961, pp 171-172t

2 - Bureau of Ships Technical Manual, Chapter 56

3 - Berry, W. C. and F. W. Fink, "Effect of Heat Transfer on Corrosion of Ferrous Alloys in Boiler Waters," Battelle Memorial Institute, 16 Apr 1963

4 - Slater, I. G. and N. L. Parr, Proc. Inst. Mech. Engrs. (London), Vol 160, 1949 pp 341-350

5 - Copson, H. R., Industrial and Engineering Chemistry, Vol. 44, Aug 1952, pp 1745-1751

6 - Hackerman, N., Industrial and Engineering Chemistry, Vol 44, Aug 1952, pp 1752-1754

7 - LaQue, F. L. and H. R. Copson, "Corrosion Resistance of Metals and Alloys," 2nd Edition, Reinhold Publishing Corp, New York, 1963

8 - Skapercas, G. and H. Uhlig, Industrial and Engineering Chemistry, Vol. 34, 1942, pp 748-754

9 - McConomy, T. A., "Standby Protection for Boilers," (paper presented at Second Annual Corrosion Control Short Course, Drexel Institute of Technology, Philadelphia, Pa., 15 Sep 1964

10 - Armetano, J. A. and V. P. Murphy, "Standby Protection of High-Pressure Boilers," (paper presented at Engineering Society of Western Pennsylvania Proceedings International Water Conference, Pittsburgh, Pa., Sep 1964

11 - Bloom, M. C., M. Krulfeld, and W. A. Fraser, Corrosion, Vol 18, No. 11, Nov 1962, pp 401-405t

12 - Bloom, M. C., M. Krulfeld, and W. A. Fraser, Corrosion, Vol. 19, Sep 1963, pp 327-330t

13 - Bloom, M. C., M. Krulfeld, and G. N. Newport, "Protective Film Formation in High Pressure Steam Generators," U. S. Patent 3,173,404, 16 Mar 1965

14 - Cheng, C. F., Corrosion, Vol. 20, Nov 1964, pp 341-349t

15 - Evans, U. R., Industrial and Engineering Chemistry, Vol. 37, No. 8, Aug 1945, pp 703-705

16 - Kahler, H. L., "Phosphate-Chromate Corrosion Protection in Water Systems," U. S. Patent 2,711,391, 21 Jun 1955

17 - Kahler, H. L. and P. J. Gaughan, Industrial and Engineering Chemistry, Vol. 44, Aug 1952, pp 1770-1774

18 - Kahler, H. L. and C. B. George, "Corrosion Inhibiting," U. S. Patent 2,872,281, 3 Feb 1959

19 - Kahler, H. L. and C. B. George, "The Dianodic Method for the Prevention of Pitting and Tuberculation," (paper presented at Engineers Society of Western Pennsylvania 11th Annual Water Conference, 16 Oct 1950, Pittsburgh, Pa.

20 - Kahler, H. L. and W. A. Tanzola, "Inhibiting Corrosion," U. S. Patent 2,900,222, 18 Aug 1959

21 - Ulmer, R. C. and J. W. Wood, Corrosion, Vol. 8, No. 12, Dec 1952, pp 402-406

22 - Ryznar, J. W. and T. R. Newman, "Corrosion Inhibiting Compositions and Method," U. S. Patent 3,151,087, 29 Sep 1964

23 - Kahler, H. L. and C. B. George, "Corrosion Inhibiting," U. S. Patent 2,793,932, 28 May 1957

24 - Hatch, G. B., "Methods of Inhibiting the Pitting of Iron and Steel," U. S. Patent 3,022,133, 20 Feb 1962

25 - Vietor, M. L., "Corrosion Inhibiting Compostions," U. S. Patent 3,141,001, 14 Jul 1964

26 - Boies, D. B., J. Crowther, and W. J. Ryzner, "Inhibition of Corrosion of Metal Surfaces in Contact with Corrosive Aqueous Media," U. S. Patent 3,081,146, 12 Mar 1963

27 - Evans, W., G. J. Fink, and H. A. Kern, "Composition for Treating the Liquid Contents of Heating and Cooling Systems," U. S. Patent 1,986,963, 8 Jan 1935

28 - Arensberg, H. G., "Water Treatment," U. S. Patent 3,099,521, 30 Jul 1963

29 - Kerst, H., "Zinc-Sodium Polyphosphate, Sodium Polyphosphate, Chelating Agent Corrosion Inhibiting Composition," U. S. Patent 3,116,105, 31 Dec 1963

30 - Lehrman, L. and H. L. Shuldener, Journal American Water Works Association, Vol. 43, No. 3, Mar 1951, pp 175-188

31 - Haering, D. W., Industrial and Engineering Chemistry, Vol. 30, No. 12, Dec 1938, pp 1356-1361

32 - Chemistry and Industry (Br), Vol. 53, 1951, pp 1194

33 - Industrial and Engineering Chemistry, Vol. 37, No. 8, Aug 1945, pp 724-735

34 - Cohen, M., R. Pyke, and P. Marier, Journal Electrochemical Society, Vol. 96, No. 4, Oct 1949, pp 254-261

35 - Allied Chemical & Dye Corporation, Solvay Process Division, "Sodium Nitrite for Rust and Corrosion Prevention"

36 - Hoar, T. P., Corrosion, Vol. 14, 1958, pp 63-64

37 - Ulmer, R. C. and J. A. Ulrich, Jr., "Method for Preventing Corrosion and Scale," U. S. Patent 2,675,351, 13 Apr 1954

38 - Darrin, M., Canadian Chemistry and Process Industries, Jun 1949, pp 512-516

39 - Wyandotte Chemical Company, Power, Jan 1964 pp 129

40 - Breston, J. N., Industrial and Engineering Chemistry, Vol. 44, No. 8, Aug 1952, pp 1755-1760

41 - NACE Technical Committee Reports, Publication 55-3, pp 195-197t

42 - Leidheiser, H. Jr., C. & E. News, 5 Apr 1965, pp 78-92

43 - Osipowe, L. I., "Corrosion Inhibition," U. S. Patent 2,890,928, 16 Jun 1959

44 - George, C. B., W. A. Tanzola and H. L. Kahler, "Corrosion Inhibiting Thiol Combination," U. S. Patent 2,877,085, 10 Mar 1959

45 - Linn, C. B. and J. A. Vesely, "Preventing Corrosion of Ferrous Metal Surfaces in Contact with Water," U. S. Patent 2,949,338, 16 Aug 1960

46 - Toekelt, W. G., "Water-Soluble Corrosion Inhibitors," U. S. Patent 2,923,599, 2 Feb 1960

47 - Levis, W. W., Jr., Wyandotte, and E. A. Weipert, "Di(alkoxyalkyl) Thiourea," U. S. Patent 3,168,560, 2 Feb 1965

48 - Pollitzer, E. L., "Preventing Corrosion," U. S. Patent 3,063,790, 13 Nov 1962

49 - Andersen, D. L. and P. E. Throckmorton, "N-Alkylheterocyclic Nitrogen-Containing Derivatives as Corrosion Inhibitors," U. S. Patent 2,993,007, 18 Jul 1961

50 - Chang, R. W. H., "Product and Process for Inhibiting Corrosion," U. S. Patent 3,036,879, 29 May 1962

51 - Cox, P. F., R. L. Every, and O. L. Riggs, Jr., _Corrosion_, Vol. 20, Sep 1964, pp 299-302t

52 - Eoins, D. B., J. Crowther, and W. J. Ryzner, "Inhibiting Corrosion with Chromium Quarternary Ammonium Salt Compositions," U. S. Patent 3,079,220, 26 Feb 1963

53 - Denman, W. L. and C. M. Hwa, "Filming Type Corrosion Inhibitor for Steam and Condensate Lines," U. S. Patent 2,889,193, 2 Jun 1959

54 - Partridge, E. P., "Treatment of Steam Systems," U. S. Patent 2,562,571, 31 Jul 1951

55 - Chittum, J. F. "Method of Inhibiting Corrosion in Steam Generating Systems," U. S. Patent 3,029,126, 10 Apr 1962

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13. ABSTRACT

    A survey of the literature was conducted to gain insight into the possibility of finding a chemical additive that will prevent corrosion in idle boilers yet still allow them to be returned to operation without first requiring draining. The mechanisms of corrosion and the important factors which affect boiler corrosion are discussed. Corrosion inhibitors are classified by the mechanisms they employ for protection. Future work to be conducted is based upon the results of this survey.

(Author)

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A. H. Wirzburger   March 1966
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conducted to gain insight into the
possibility of finding a chemical
additive that will prevent corrosion
in idle boilers yet still allow them
to be returned to operation without
first requiring draining. The mech-
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4. Processes,
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factors which affect boiler corrosion are discussed.
Corrosion inhibitors are classified by the mechanisms
they employ for protection. Future work to be conducted
is based upon the results of this survey.